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by

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Krishna Rajan, and John Hudson

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DECOMPOSITION KINETICS AND FILM FORMATION OF AN

ORGANOMETALLIC PRECURSOR TO SiC ON Si(100)

by

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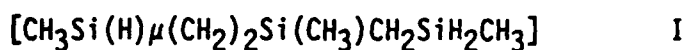WEI LEE AND LEONARD INTERRANTE

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ABSTRACT

The adsorption and decomposition kinetics of the SiC precursor

$$[CH_3Si(H)\mu(CH_2)_2Si(CH_3)CH_2SiH_2CH_3] \qquad \text{I}$$

have been studied on the Si(100) surface using a combination of molecular beam mass spectrometry and Auger electron spectroscopy. The intact precursor adsorbes with a heat of adsorption of about 10 kcal/mol. The decomposition rate becomes measurable at about 800 K, and increases with increasing temperatures. The resulting films are stoichiometric, polycrystalline SiC, with partial epitaxial orientation relative to the substrate.

I. INTRODUCTION

The synthesis of organometallic precursors to solid materials is an area of rapidly increasing interest in both the electronic and structural materials areas. These materials (Precursors) offer the ability to produce high melting point materials, of good stoichiometry and crystallinity, at temperatures far below the melting points of the materials produced. Although the techniques for synthesizing these precursors are highly advanced, and some studies have been made of how these molecules decompose in the gas phase, very little is known about the decomposition kinetics and decomposition pathways on preexisting solid surfaces.

We report here initial studies of the decomposition of the silicon carbide precursor


I
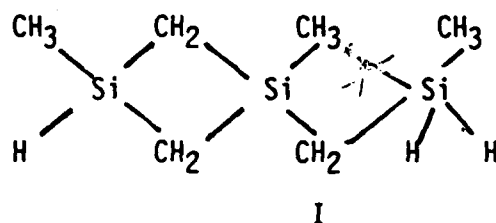
on a clean Si(100) surface, using the techniques of molecular beam mass spectrometry and Auger electron spectroscopy. Results indicate that stoichiometric, microcrystalline films can be grown at temperatures as low as 600°C, but that the expected gas-phase reaction products were not observed.
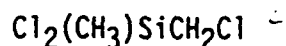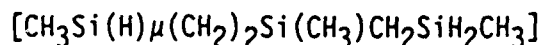
II. EXPERIMENTAL

A: Precursor Species

The precursor,

$$[CH_3Si(H)\mu(CH_2)_2Si(CH_3)CH_2SiH_2CH_3] \qquad I$$
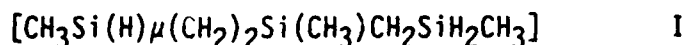
was synthesized using choromethyl chlorosilane coupling reactions, reacting

$$Cl_2(CH_3)SiCH_2Cl$$

with magnesium followed by reduction with LiAl H_4.[1] After purification, the precursor was characterized by mass spectrometry, FTIR spectroscopy and NMR spectroscopy. This latter technique indicated that the final product consisted of two stereoisomers of compound I,

$$[CH_3Si(H)\mu(CH_2)_2Si(CH_3)CH_2SiH_2CH_3]$$

in roughly equal proportions.

B: <u>Experimental System</u>

Reaction kinetic measurements were carried out in an all metal ultra-high vacuum system, shown schematically in Figure 1. This system, which was previously used for reactive molecular beam scattering studies of simple molecules,[2,3] consists of a cylindrical main chamber, in which the Si(100) sample was mounted on axis, on a positioner which allows motion in three orthogonal directions plus rotation about the chamber axis. The sample could be heated by electron bombardment from an enclosed filament to 1200 K and cooled by conduction to a LN_2-cooled cold finger to 130 K. The sample could be cleaned by standard argon ion bombardment and anneal techniques.

The main chamber also contained a cylindrical mirror analyser based system for Auger electron spectrometry and a doubly deferentially pumped

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quadrupole mass spectrometer, located with a line-of-sight to the sample. The main chamber also contained a second mass spectrometer, which could provide information on residual gases and unreacted precursor species.

The precursor was admitted through a solenoid operated pulsed valve. This valve was built in house, and was constructed so that only stainless steel, high purity iron and Viton contacted the precursor species. The valve produced a pulse of gas with a FWHM of roughly one millisecond. The repetition rate was variable from below one Hz to 20Hz. The pulse amplitude depended primarily on the pressure behind the valve, which in this work was the equilibrium vapor pressure of the precursor species at room temperature; roughly 2 Torr.

C. Reaction Kinetic Measurements

    1. Precursor Mass Spectrum.

        The mass spectrum of the precursor in the detector mass spectrometer was first obtained by allowing the pulsed valve to operate for an extended period with the sample at room temperature, (Later studies show that in this case the decomposition rate is essentially zero) while the detector mass spectrometer was swept over the available mass range. The results of this measurement are shown in Figure 2, along with a reference spectrum of the same material obtained using a conventional analytical mass spectrometer.[1] The results for the two spectrometers are similar, except that the mass range of the detector in our system is limited to ≈ 100 AMU.

    2. Physical Adsorption of Precursor

        Two sets of measurements were made at low temperature to characterize the adsorption behavior of the intact precursor. In one set of measurements, the sample was cooled to 130 K, and the pulse valve

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operated for 100 to 5000 pulses. The sample was then heated at a linear rate of about 5 $K/_{sec}$ and one of the precursor mass peaks monitored on the detector mass spectrometer, producing a typical thermal desorption spectrum. The results of a series of these measurements, with varying exposures, are shown in Figure 3. In all cases two desorption peaks were observed.

The second set of low temperature measurements involved operating the pulse valve with the sample at a somewhat higher temperature, and collecting the resulting waveform of signal vs time on the detector mass spectrometer, tuned to mass 73. Typical results are shown in Figure 4. Note that at the lowest temperature shown, the signal is greatly attenuated due to the long surface life time of the precursor. As the temperature is raised, the wave form approaches that of the pulse valve, convoluted with the pumping time constant of the main chamber.

3. Decomposition Kinetics

Here again, two types of measurement were made. In one set of measurements, waveforms were obtained for the mass 73 peak, as described above, but at increasing substrate temperatures. For temperatures above about 400 K, all waveforms had essentially the same shape. At higher temperatures, the amplitude of the waveform was attenuated due to decomposition of the precursor on the surface. This trend is shown in Figure 5, where the data have been corrected for the difference in mass spectrometer sensitivity as a function of gas temperature.

Attempts were also made to detect waveforms of the expected gas-phase product species, such as CH_3, CH_4, C_2H_6, and H_2. No signal coherent with the pulsing process was observed at any of these

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masses. In the case of H_2, the background in the detector would have hidden the expected signal. In the case of the other masses, if a peak comparable to the reduction in the mass 73 peak had been present, it would have been observed. This indicates either that the excess C and H are eliminated through some other channel, or that the desorption rate of product species is slow compared to the pulse width.

D. Auger Spectrometric Measurements

Auger spectra taken before exposure to the precursor species showed only peaks attributable to silicon. This was also the case after exposure to precursor at temperatures below 750 K. After exposure at higher temperature, a carbon peak was also visible, with a carbon tc silicon ratio consistent with the formation of a SiC layer on the sample surface.

E. Ex-Situ Measurements

At the conclusion of the kinetic measurements, two samples were further investigated by scanning electron microscopy and transmission electron microscopy.

Typical SEM results are shown in Figures 6 and 7. These micrographs were taken on that part of the sample that was exposed to the precursor beam. Micrographs of areas that were masked from the precursor beam were completely featureless. Figure 6, taken at a magnification of 5000, shows numerous small features, crystallographically aligned with the substrate. Figure 7, taken at a higher magnification of 15000, suggests that these features are etch features, and that a thin film has grown on the surface, as indicated by the spiral patterns on the micrograph. In some cases, the film extends over the etched area, suggesting that the etching took place after the film was deposited.

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One sample was thinned electrochemically and examined by transmission electron microscopy. An image of this film is shown in Figure 9. It shows a polycrystalline array of grains, with an average grain size and about 0.05μm. These grains are heavily faulted and twinned, suggesting that the cubic and hexagonal forms of SiC may coexist in the film. This interpretation is based on the fact that twins in a cubic strucuture are essentially structural precursors in the cubic → hexagonal transformation.

A selected area diffraction pattern taken from this same film is shown in Figure 9. The diffraction pattern is consistent with a polycrystalline film of SiC.[4] It is apparent that there is some preferred orientation in the film, with <111> SiC || <111>Si. While the growth mode is not completely epitaxial, it is significant that some degree of lattice matching is occurring, even at the low deposition temperatures used here.

III. DISCUSSION

Taken together, the results reported above provide a great deal of information on the interaction of the precursor with the surface.

The fact that the scattered precursor signal was reduced to background levels at low surface temperature indicated efficient accommodation of all precursors into a physisorbed state. The two peaks observed in the thermal desorption experiment are consistent with the observation by NMR that the sample consisted of two stereoisomers, in roughly equal proportions.

Because of difficulties with the temperature measurement system, it was not possible to determine adsorption energies from the TDS data. Analysis of the trailing edge of the transients observed in the isothermal measurements at and below ambient temperature indicated a heat of

desorption of about 10 Kcal/mol.

The waveform data taken at higher substrate temperatures clearly indicate the onset of precursor decomposition at about 800 K. At the highest temperature studied, 940 K, the single collision reaction probability has risen to about 0.15, with no signs of saturation. In our apparatus, visible transient signals would be observed for peaks less than 10% of the amplitude of the peaks used for these measurement (mass 73). Thus, if the surface decomposition reaction produced hydrocarbon species that desorbed promptly into the gas phase, these desorbed products species should have given rise to measurable mass spectrometer transients at the appropriate mass. No such transients were observed. One possible reason for the failure to observe these transients could be a sluggish surface reaction or desorption process, which would have attenuated the amplitude of the transient. In view of the short surface lifetime of the precursor at these temperatures (extrapolated from our low temperature measurement), and the expected much shorter surface lifetime for simple hydrocarbons, this reason is unlikely. The alternative explanation is that the excess hydrocarbon material reacts with the silicon substrate to produce additional SiC. This explanation is consistent both with the observation by Auger electron spectroscopy that the film is essentially stoichiometric SiC and that the surface of the silicon sample showed etch features after the film formation process.

Finally, it should be noted that the films produced were grown in the course of the kinetic studies. Thus the nucleation and growth conditions are not well defined. Further studies, in which the sample temperature and precursor impingement rate are varied systematically are required to determine the effect of these variables on film morphology.

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The effect of gas-phase heating of the precursor, with the accompanying possibility of gas-phase decomposition prior to impingement on the substrate, should also be investigated.
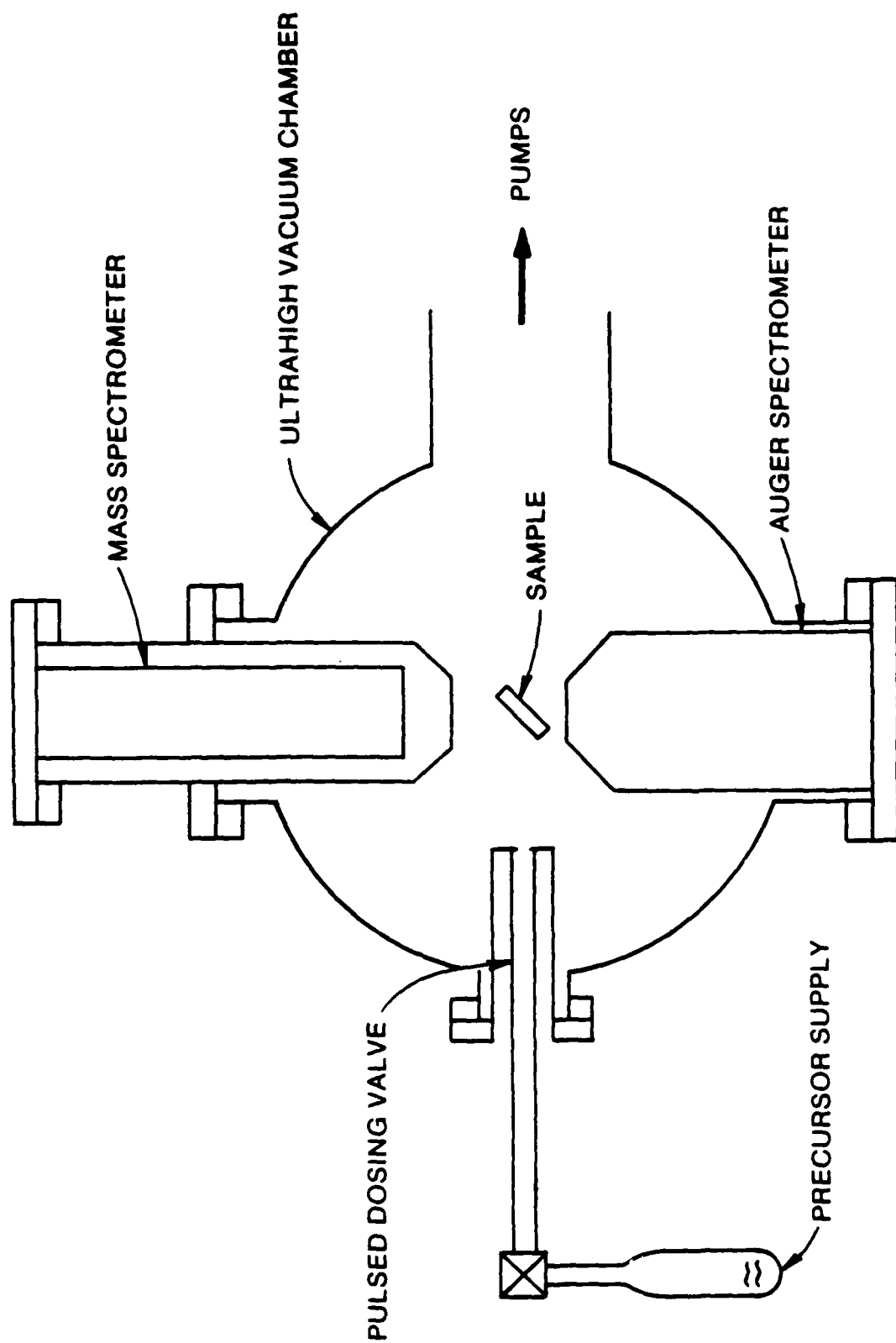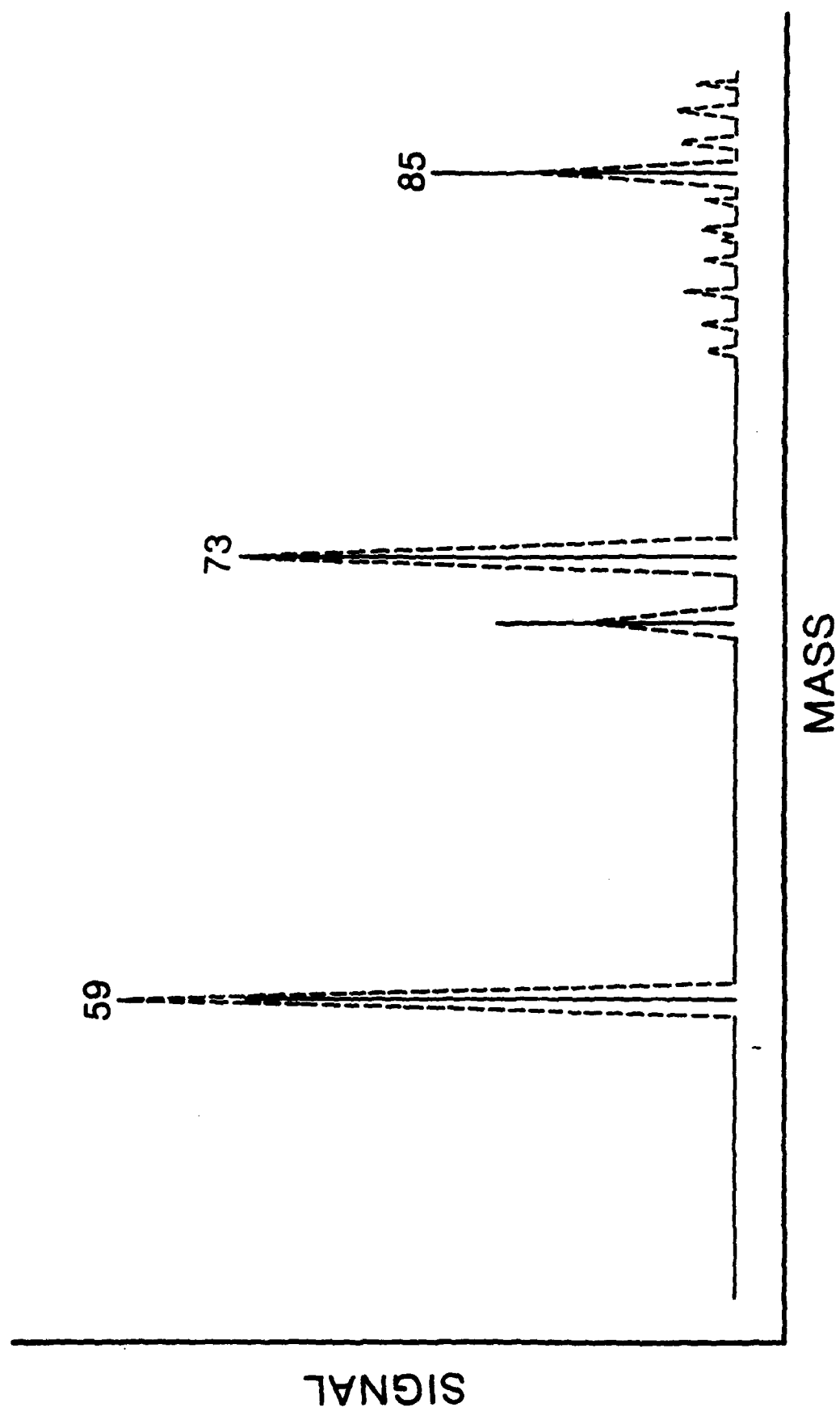
ACKNOWLEDGEMENTS

FIGURE CAPTIONS

Figure 1:   Schematic diagram of the molecular beam system used for kinetic stitches

Figure 2:   Comparison of the mass spectrum observed for the intact precursor model, using the mass spectrometer on the molecular beam system, with the corresponding mass spectrum taken with an analytical mass spectrometer. The two spectra are normalized at $m/e = 73$.

Figure 3:   Thermal desorption spectra obtained after adsorption of the precursor on the clean Si(100) surface at $T \approx 130K$. The numbers indicate the total precursor dose, in terms of the number of pulses from the pulsed dosing valve.

Figure 4:   Desorption transients observed during dosing of precursor onto the clean Si(100) surface, for various surface temperatures.

Figure 5:   Dependence of the scattered signal amplitude on temperature for the precursor on Si(100). The drop off above 800 K indicates an increasing surface decomposition probability.

Figure 6:   Scanning electron micrograph of the sample surface after removal from the vacuum system subsequent to kinetic experiments. Magnification : 500X.

Figure 7:   Scanning electron micrograph of the sample surface. As above, but at a magnification of 1500X. Etched areas on the silicon and spiral growth patterns of the film are apparent.

Figure 8:   Transmission electron micrograph of the SiC film formed by precursor decomposition. Note the many turns and stacking faults.

Figure 9 :   Selected area electron diffraction patterns from the film shown in Figure 9. Note the partial epitaxial relationship with <111> SiC $\parallel$ <111> Si.
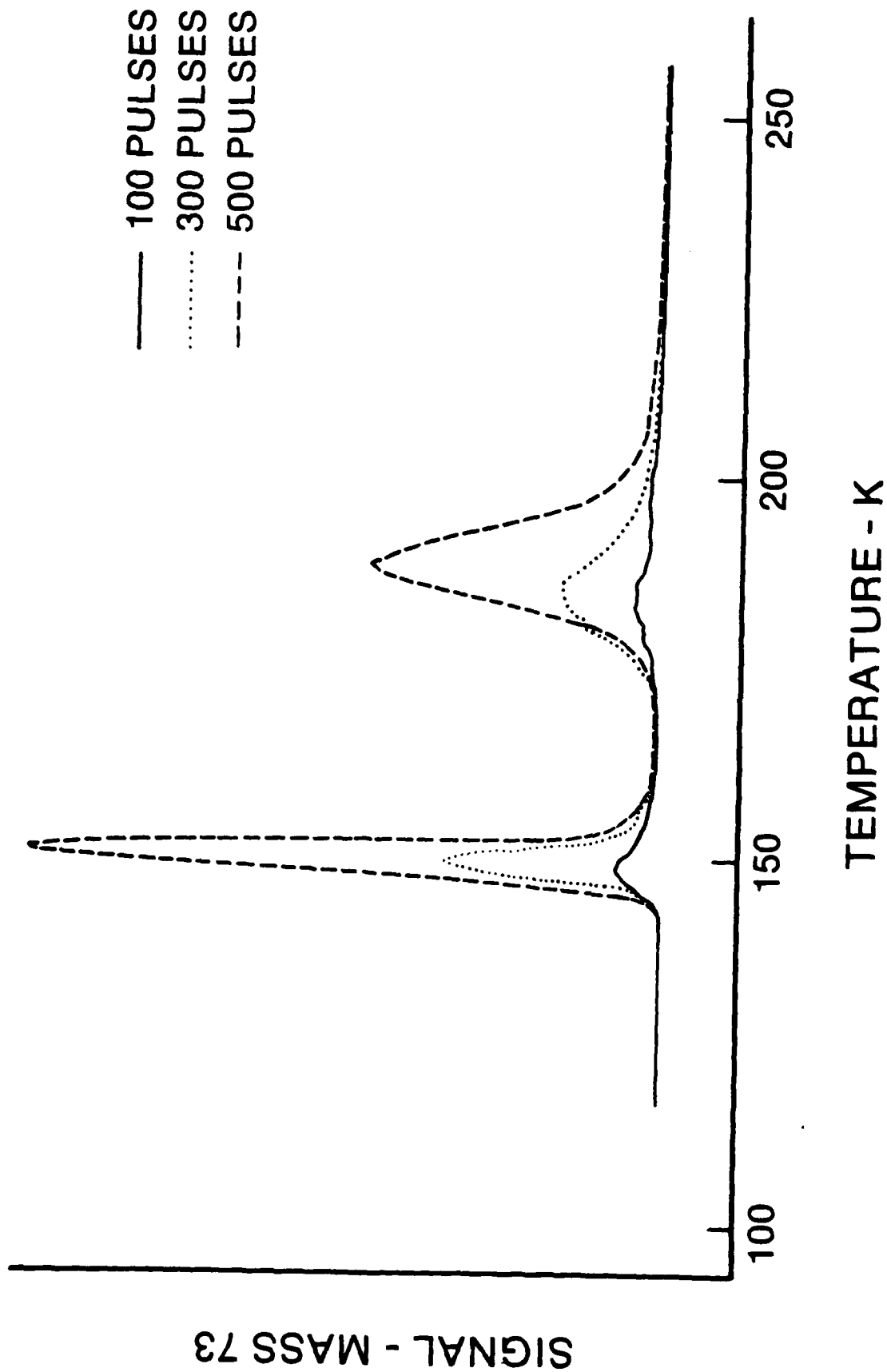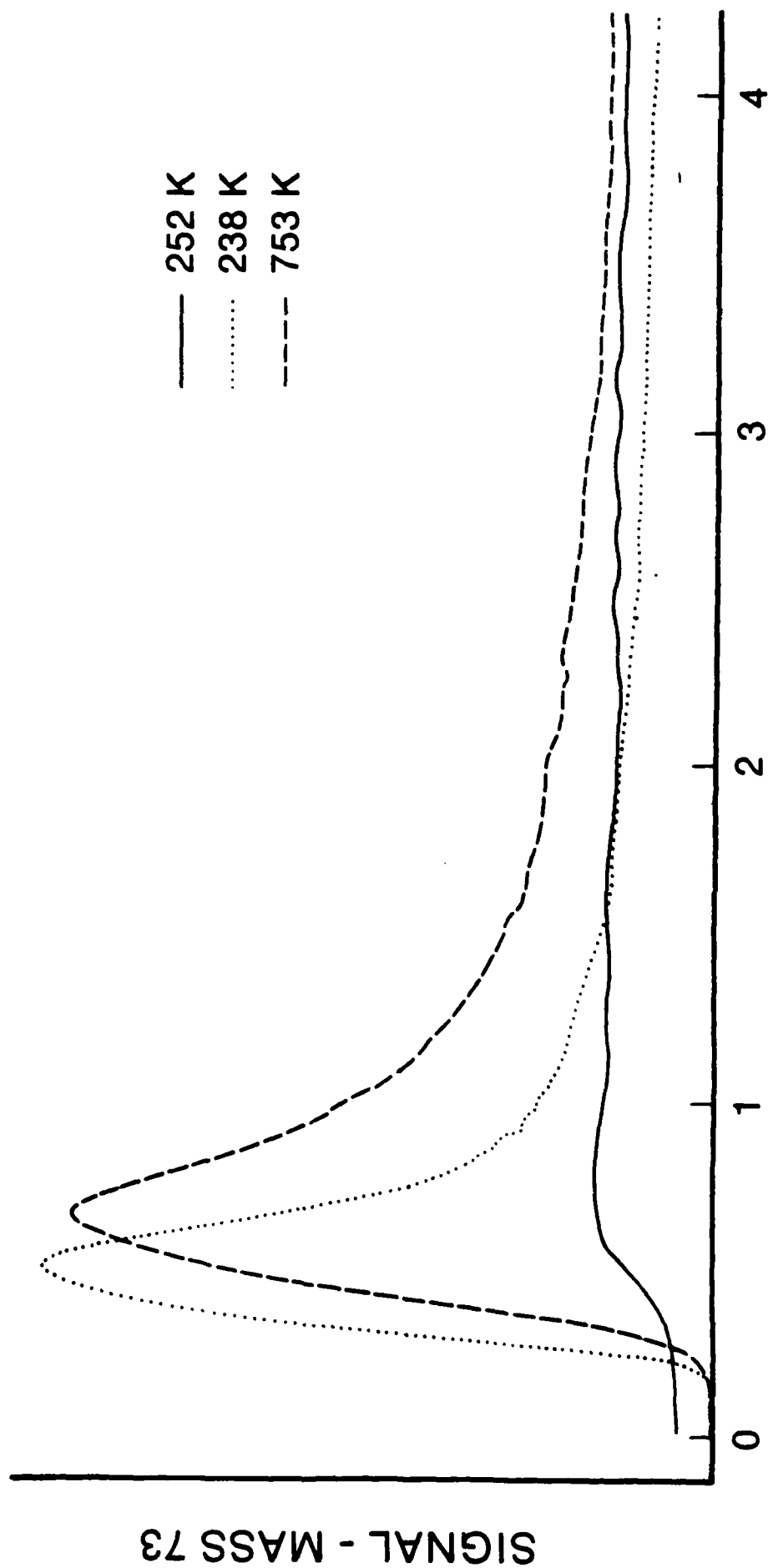
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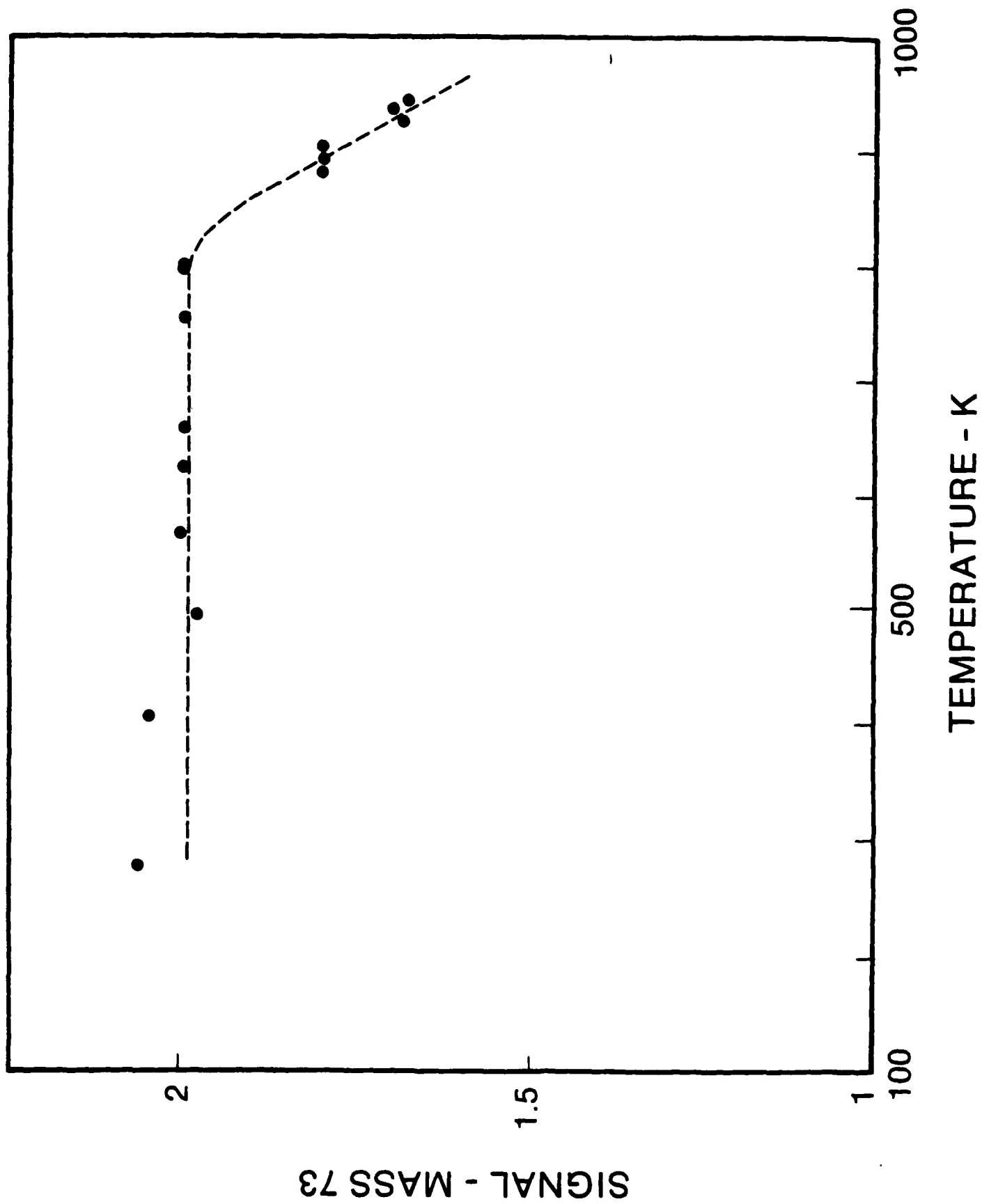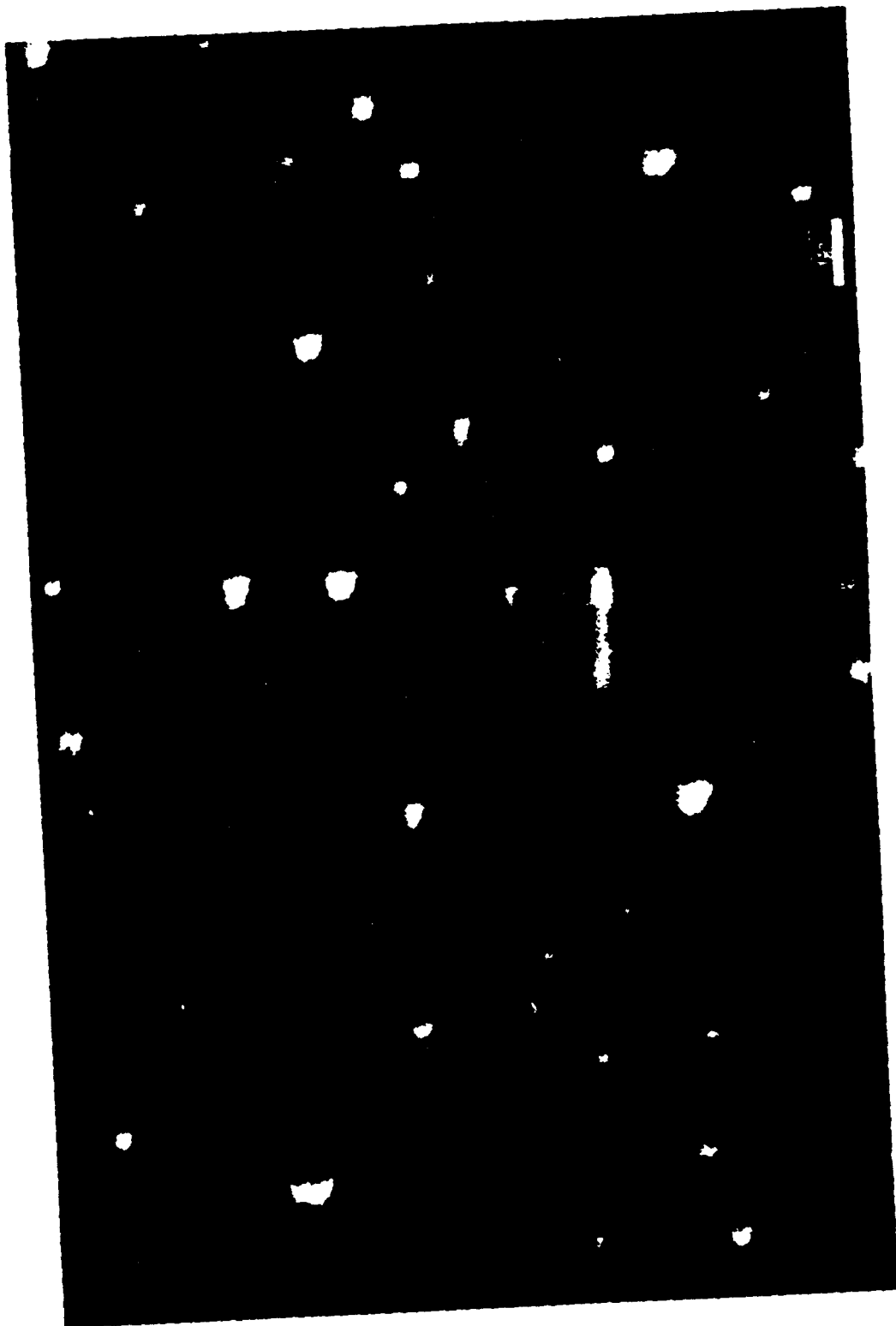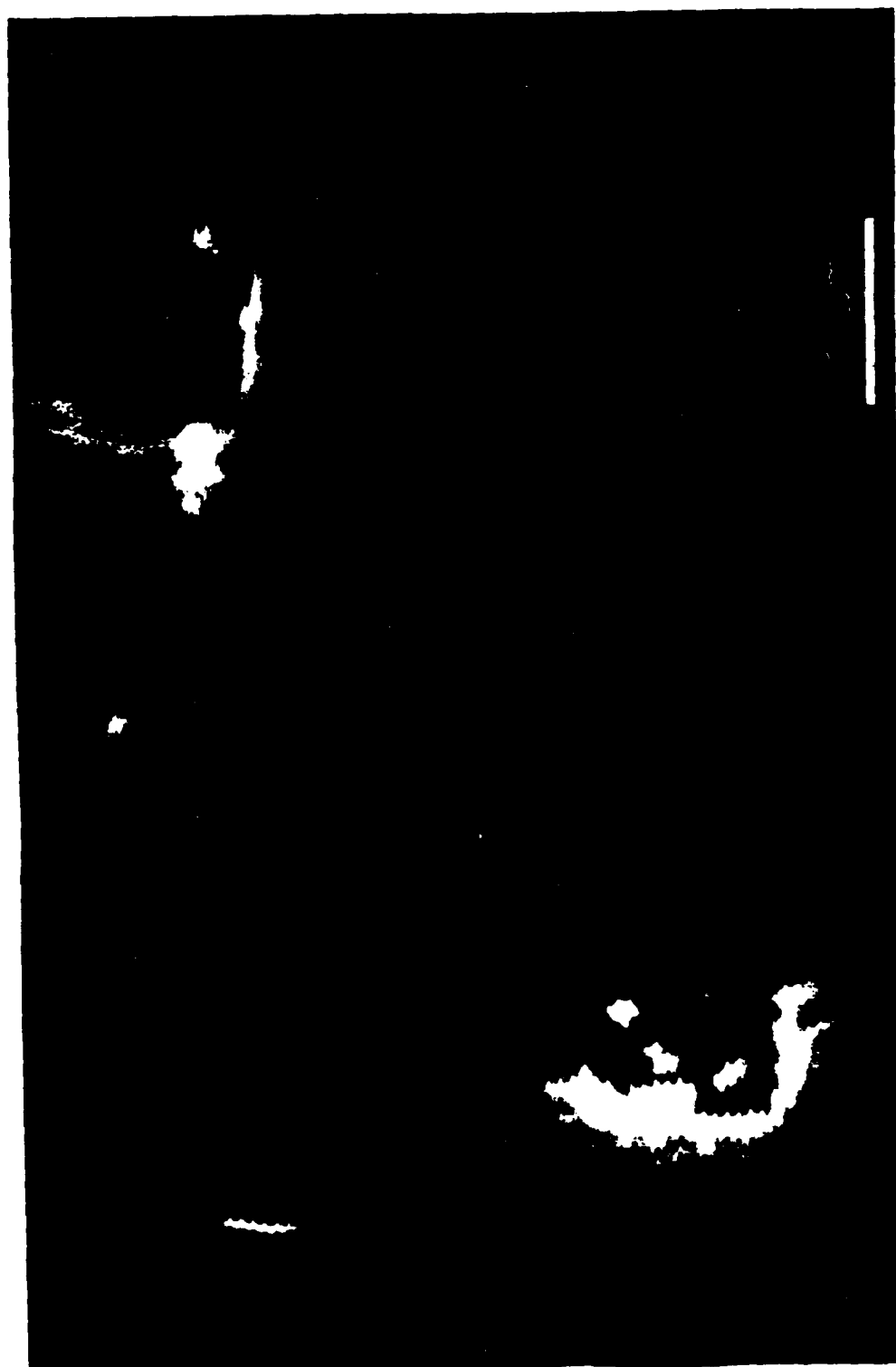
K. LENZ, J.B. HUDSON et al – FIGURE 1

MASS SPECTROMETER

ULTRAHIGH VACUUM CHAMBER

PUMPS

SAMPLE

AUGER SPECTROMETER

PULSED DOSING VALVE

PRECURSOR SUPPLY

K. LENZ, J.B. HUDSON et al - FIGURE 2

K. LEWIS, J. B. HUDSON et al - FIGURE 3

100 PULSES
300 PULSES
500 PULSES

TEMPERATURE - K

SIGNAL - MASS 73

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SIGNAL - MASS 73

252 K
238 K
753 K

R. LENE, J.B. HUDSON et al - FIGURE 5

SIGNAL - MASS 73

TEMPERATURE - K

FIGURE 6

FIGURE 7

FIGURE 8

Figure 9